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Low-Absorption Laser Windows

Semiannual Report 1
for Period Ending 31 December 1975

P. H. KLEIN, editor

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P. H. Klein
(202)767-3671

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This semiannual report summarizes work by NRL under ARPA Order 3066. Improvements have continued in methods for preparation, surface finishing, and characterization of low-loss laser-window materials. Calorimetric absorption studies included measurements of eight alkali and alkaline earth halides at 1.06 micrometers and of calcium fluoride, zinc selenide, and several alkali halides at 2.7, 3.8, and 10.6 micrometers. Adequate surface preparation virtually eliminates detectable surface absorption. Carbon tetrachloride is the most effective reactive halide for purification of potassium

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20. Abstract (Continued)

bromide, which was shown by bulk absorption coefficients for KBr as low as 0.000003 per centimeter at 1.06 micrometers and 0.000014 per centimeter at 10.6 micrometers (but nevertheless 0.0001 to 0.0002 per centimeter at 2.7 and 3.8 micrometers) and by the absence of metaborate ions in the crystals. A polishing method analogous to that for KCl was found effective for KBr, resulting in pit-free surfaces stable to room air for over a week, especially for surfaces remote from cleavage planes. Appended to this report is an abstract of a Navy-sponsored paper which compares crack propagation in alkali halides with that in alkaline earth fluorides. Future studies (for which some crystals have been prepared) will involve purification of strontium fluoride, additive strengthening of potassium chloride and potassium bromide, and testing of an evacuated calorimeter.

CONTENTS

FOREWORD

This semiannual technical report summarizes work performed by personnel of the U. S. Naval Research Laboratory, Washington, D.C. 20375, under ARPA Order 3056. The program was coordinated by Dr. P. H. Klein of NRL, and monitored by Dr. C. M. Stickley and CAPT H. Winsor of ARPA. The report covers the period from 1 July 1975 through 31 December 1975. The publications and presentations listed on the following page illustrate several of the recent results of this program. Some material from Navy-supported programs is included in the report for the interest of those concerned with laser windows.

PUBLICATIONS AND RECENT PRESENTATIONS

Presented at Fifth Conference on Infrared Laser Window Materials, Las Vegas, NV, 1-4 December 1975, and submitted for publication in the Proceedings.

a. Klein, P. H., Growth of Lowloss KBr in Halide Atmospheres.

b. Davisson, J. W., Chemical Polishing of KBr and Absorption Measurements at 1.06 μm.

c. Rosenstock, H. B., Gregory, D., and Harrington, J. A., Bulk and Surface Absorption by Analysis of Laser Calorimetric Data.

d. Freiman, S. W., Becher, P. F., Rice, R. W., and Subramanian, K. N., Fracture Behavior in Alkaline Earth Fluorides.

LOW-ABSORPTION LASER WINDOWS

Semiannual Report 1
for Period Ending 31 December 1975

INTRODUCTION AND SUMMARY

Improvements have continued to be made in methods for preparation, surface-finishing, and characterization of lowloss laser-window materials. This work, under ARPA Order 3066, is a direct outgrowth of that begun under ARPA Order 2031. (The two programs were, in fact, concurrent during the first three months of this reporting period.) Summarized below are results of work sponsored by ARPA during the reporting period, along with some pertinent results obtained under Navy sponsorship.

Carbon tetrachloride has been shown to be the most effective reactive halide for purification of potassium bromide. Absorption coefficients as low as 1.4×10^{-5} cm^{-1} at 10.6 μm and 3×10^{-6} cm^{-1} at 1.06 μm have been measured in crystals purified with CCl_4. That CCl_4 was the most effective of the reactive halides studied was also demonstrated by the absence of metaborate ion (BO_2^-) from crystals processed in CCl_4, as shown by infrared spectra. Despite its effectiveness in removing oxygen-containing impurities, the absorption of CCl_4-purified KBr at 2.7 and 3.8 μm remains in the 0.0001-0.0002 cm^{-1} range - approximately one order of magnitude higher than indicated by its absorption at 1.06 and 10.6 μm.

A method of polishing analogous to that for KCl has been found effective for KBr. After water-grinding, crystals are polished, successively, in fuming HBr (for 30 minutes) and in a 1:1 diluted solution of HBr (for 30 seconds). Rinsing in 2-propanol and drying in warm air yields smooth, pit-free surfaces which are stable to laboratory air for more than a week. The procedure is most effective for surfaces whose orientation is remote from cleavage planes.

Laser-calorimetric absorption studies have included measurements of eight alkali and alkaline-earth halides at 1.06 μm. When purity is adequate, most of these substances have bulk absorption coefficients between 5×10^{-6} cm^{-1} and 5×10^{-5} cm^{-1} at this wavelength. Adequate surface preparation virtually eliminates detectable surface absorption. A KBr crystal that had been purified in CCl_4 vapor showed a bulk absorption coefficient of less than 3×10^{-6} cm^{-1} - at or below the limits of sensitivity of the calorimeter.

Other absorption studies, at 2.7, 3.8, and 10.6 μm, were carried out on calcium fluoride, zinc selenide, and several alkali halides. Variations of sample temperature with time during and after laser heating were fitted with "best" values of bulk absorption coefficient, surface absorption, and heat-transfer coefficient. Excessive sample-to-sample variations were attributed mainly to variations in surface quality.

Results of these studies were reported at the Fifth Laser Window Conference at Las Vegas, NV, during early December 1975. Preprints of the papers submitted for the Proceedings of that Conference are included as appendices. Also appended is the abstract of a paper on fracture behavior of alkaline-earth fluorides. This work, under Navy sponsorship, is of interest because it compares crack propagation in alkali halides with that in alkaline-earth fluorides.

Plans for the next period include purification of SrF_2 in reactive atmospheres, and measurement of its absorption. Studies of additive strengthening will include investigation of the effects of addition of up to two mol per cent of sodium and rubidium to potassium chloride, as well as addition of strontium or lanthanum to potassium bromide. (Some of the crystals for these investigations have already been prepared.) Calorimetric measurement techniques will be ref_ned to include testing of an evacuated calorimeter.

GROWTH OF LOWLOSS KBr IN HALIDE ATMOSPHERES*

Philipp H. Klein
Naval Research Laboratory
Washington, DC 20375

ABSTRACT

Potassium bromide single crystals have been prepared with 10.6-μm bulk absorption coefficients smaller than the intrinsic value for potassium chloride. Of several halogen-producing vapors studied, that of carbon tetrachloride is most effective in decreasing infrared absorption. Hydroxyl lines are absent from infrared absorption spectra of all crystals, although vacuum-ultraviolet absorption at 215 nm corresponds to presence of from 0.01 to 4.0 OH^- ions per million anions. Incomplete removal of metaborate (BO_2^-) contamination by iodine monobromide or by hexabromobenzene is evident in infrared absorption spectra.

I. INTRODUCTION

Potassium bromide, with intrinsic 10.6-μm absorption coefficient less than 0.00001 cm^{-1} (1), is a logical next step in decreasing losses in laser-window materials. It can be handled with much the same equipment as can potassium chloride, for which intrinsic absorption at 10.6 μm (0.0001 cm^{-1}) has been demonstrated (2). Its melting point (734°C) is fairly close to that of KCl (771°C) (3). It should be amenable to reactive-halide purification. Its optical properties are well-known (4). Its hygroscopicity is debatable, but thought to be tractable, in any case. Reactive-halide purification of KBr was therefore undertaken.

II. REACTIVE HALIDES

There is evidence that oxygen-containing impurities are involved in extrinsic absorption processes in the 10.6-μm region (5). Hydroxyl ion has received wide attention because its removal from potassium halides (KX) tends to decrease their 10.6-μm absorption. Prevention of hydrolysis of KX should tend to diminish this absorption.

It may be assumed that OH^- will not contribute to optical absorption if its concentration is sufficiently low. The equilibrium, $KX + H_2O = KOH + HX$, must therefore be displaced to the left. This displacement is natural at room temperature,

where the equilibrium constant (3) is 2.6 X 10^{-29} for hydrolysis of KCl, and 1.1 X 10^{-31} for that of KBr. At $1100^{\circ}K$, above the melting points of the salts, the equilibria still favor the halides, but not as strongly: for KCl, K = 6.4 X 10^{-8}; and, for KBr, K = 1.3 X 10^{-8}.

Let us apply these equilibrium constants to halides in an inert atmosphere whose relative humidity at $25^{\circ}C$ is 50 per cent, a water-vapor partial pressure of 12 torr (0.016 atm). One mole of KCl confined in two molar volumes of this wet gas at $1100^{\circ}K$ ($827^{\circ}C$) will yield at equilibrium 2 X 10^{-9} moles of KOH. With KBr, 4 X 10^{-10} moles of KOH will be formed.

Hydrolytic contamination during processing can be controlled by maintenance of a partial pressure of HX which exceeds the equilibrium value. For the examples here, that partial pressure is never greater than 10^{-9} atm (7.6 X 10^{-7} torr).

Both organic and inorganic compounds are capable of reacting with potassium hydroxide to yield a potassium halide, a hydrogen halide, and some oxygen-containing residue. In Table 1, conversion of one mole of KOH to one mole of potassium halide is considered. For each mole of KX formed, one mole of HX is also produced. Therefore, every reaction in Table 1 not only removes OH^- but also tends to prevent its reintroduction by hydrolysis.

Equilibrium constants are also shown for the reactions of Table 1. Listed organic halides are seen to be more effective than are inorganic bromides. Equilibrium constants are within an order of magnitude for most bromides and corresponding chlorides. Reactions producing carbon monoxide are the most effective at elevated temperatures.

The list of reactions in Table 1 is not exhaustive. Some highly-favored equilibria may have been omitted. In addition, because products of some reactions can serve as reagents in others, comparisons should include both reaction steps. Finally, vapor pressures of reagents are not considered. Of the compounds listed in Table 2, only IBr and CCl_4 have appreciable vapor pressures near room temperature. If heated, all considered reagents should nevertheless diminish OH^- contamination.

III. EXPERIMENTAL

High-purity KBr was used for final studies, reagent-grade chemicals being used for all other purposes. The apparatus was essentially that used previously (2), except that a heated Teflon side-arm was provided at the inlet to the

Table 1. Standard Free Energies of OH⁻-Removing Reactions

		Log_{10}(Eq. Const.) at T =		
Reaction	Halogenating Agent	$298°K$ $25°C$	$900°K$ $627°C$	$1000°K$ $727°C$
$XY + KOH =$	Br_2 (X=Y)	9.62	5.37	5.08
$KX + 1/2\ O_2 + HY$	IBr (X=Br)	0.61	2.01	2.04
	IBR (X=I)	0.20	1.97	2.01
$1/2\ CX_4 + KOH =$	CBr_4	47.34	20.01	18.59
$KX + 1/2\ CO_2 + HX$	CCl_4	51.78	21.28	19.92
$2\ CX_4 + KOH =$	CBr_4	16.68	6.81	6.36
$KX + 1/2\ O_2 + HX + C_2X_6$	CCl_4	11.87	6.25	5.70
$CX_4 + KOH =$	CBr_4	39.95	22.78	21.87
$KX + CO + HX + X_2$	CCl_4	36.55	21.72	21.12
$1/2\ C_2X_6 + KOH =$	C_2Br_6	36.42	21.85	21.24
$KX + CO + HX + 1/2\ X_2$	C_2Cl_6	41.58	23.08	22.51
$C_2X_6 + KOH =$	C_2Br_6	39.19	26.99	26.93
$KX + CO + HX + 2\ X_2 + C$	C_2Cl_6	37.20	26.08	26.07
$1/3\ C_6Br_6 + KOH =$	C_6Br_6	42.32	21.57	20.49
$KBr + CO + HBr + C$				

Table 2. Vapor Pressures of Halides Listed in Table 1.[a]

Halide	P =	Temperature (°C) at which 1	10	100	760 torr
IBr			(25)		116
CCl_4		-50	-20	23	77
CBr_4			(60)	120	190
C_2Cl_6		33	74	110	174
C_6Cl_6		114	166	235	309

[a]D. R. Stull, Ind. Eng. Chem. **39**, 517 (1947).

reaction chamber. Solid halogenating agents were placed within this side-arm. The temperature was adjusted to provide a vapor pressure of no more than 100 torr, approximately the room-temperature vapor pressure of carbon tetrachloride. This partial pressure was considered adequate because it had proved effective in preparation of lowloss KCl (2).

Vacuum-dried KBr was contained in a Vycor Bridgman crucible within the reaction chamber. The chamber temperature was raised to 600°C, titanium-gettered argon being the flowing ambient gas. Exposure to halogenating vapors began at this temperature, which was maintained for several hours. (In the case of carbon tetrachloride, vapor was entrained for three five-minute exposures of the salt to the halogenator. Vapors of bromine-containing agents were allowed to flow continuously.)

Crystals were grown with a diameter of 2.5 cm and lengths up to 10 cm. The top two or three centimeters were cloudy, and sometimes cracked or otherwise unfit for measurement. Carbon, when it appeared, was exclusively within or atop this region. Samples treated with CCl_4 slid easily from the crucible, as did some grown in IBr. Sticking was noticeable when C_2Br_6 or C_6Br_6 were the sources of halogen. Crystals grown in CBr_4 vapors were badly cracked and stuck to the crucible.

Samples were prepared for spectrophotometry and for laser calorimetry by the methods of Davisson (6). All spectrophotometric measurements employed double-beam instruments. Laser calorimetry at both 1.06 and 10.6 micrometers was performed with the apparatus of Ref. 2.

IV.   RESULTS AND DISCUSSION

One measure of the general impurity content of a crystal is its absorption in the multiphonon region of the infrared (1). In pure crystals, the absorption coefficient decreases exponentially with increasing energy. Table 3 indicates that all crystals produced are comparable to that studied by Deutsch (1). The action of all purifying agents is roughly equivalent in this spectral region.

Sharp-line spectra can be used to estimate hydroxyl content. None of the specimens showed perceptible OH⁻ absorption lines in the 2.7-2.8-micrometer region. Nevertheless, OH⁻ content can be determined from absorption at 215 nm, in the vacuum ultraviolet. At this wavelength, the absorption coefficient increases by 1.0 cm⁻¹ for each 2.5 OH⁻ ions per million anions (ppmA) (7). Results of 215-nm measurements of OH⁻ concentrations appear in the second column of Table 4.

6

Table 3. Multiphonon-Region Absorption in KBr.

| | Absorption Coefficient in cm^{-1} | | |
Reagent $\mu =$	350 cm^{-1}	400 cm^{-1}	450 cm^{-1}
IBr	0.72	0.20	0.043
C_2Br_6	0.88	0.70	0.09
C_6Br_6	0.70	0.28	0.12
CCl_4	0.84	0.27	0.057
---	0.9[a]	0.26[a]	0.075[a]

[a] T.F. Deutsch, J. Phys. Chem. Solids 34, 2091-2104 (1973)

Table 4. Bulk Absorption Coefficients at Laser Wavelengths.

| | (OH^-), | β in units of 10^{-5} cm^{-1} at: | | | |
Reagent	ppmA	1.06	2.7	3.8	10.6 μm
IBr	0.05	2.	--	--	20.
C_2Br_6	0.07	3.	--	--	20.
CCl_4	0.05	0.5	12.[a]	17.[a]	6.
CCl_4	<0.01	0.3	12.[a]	22.[a]	1.4

[a] Data of J. A. Harrington, University of Alabama at Huntsville.

The crystal listed in the last line of the table had an absorption at 215 nm that could barely be discerned.

The expected correlation between hydroxyl content and 10.6-μm absorption is not evident in Table 4. Crystals grown in brominating atmospheres have similar properties, according to the table. Absorption of the crystals treated with carbon tetrachloride vapor is about the same at all wavelengths except 10.6 μm. Only there does the diminished OH^- content of the last listed crystal appear to have some effect. A possible explanation may be the presence of another, unspecified impurity.

Evidence for contamination by other anions is the series of lines found in the otherwise featureless spectra of

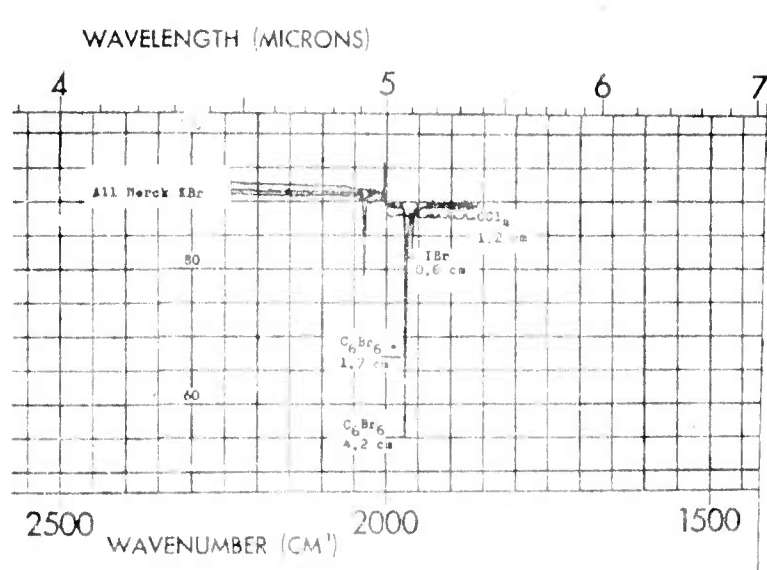crystals grown in IBr and C_6Br_6. These are shown in Figure 1.

Figure 1. Sharp-line spectrum of crystals processed in iodine monobromide or hexabromo-benzene. Optical path-lengths are indicated. Lines are absent from spectrum of crystal treated with carbon tetrachloride.

These lines, as well as those at 16.4 and 17.0 μm, have been identified as due to presence of potassium metaborate (KBO_2) (8). Their complete absence from spectra of crystals produced in other halogenating agents will be considered here.

Duthler (5) has found several anions whose presence in amounts as small as 100 ppm should result in absorption coefficients greater than 0.0001 cm^{-1} at 10.6 μm. Perchlorate, carbonate, sulfate, and metaborate are prominent among those listed. In Table 5 are shown the 1000-degree equilibrium constants for a number of reactions which remove these contaminants. Potassium perchlorate, it is seen, decomposes spontaneously. Reaction with carbon tetrachloride volatilizes oxygen-containing residues, in the cases of carbonate and sulfate contamination. With metaborate contamination, volatilization of oxygenated products requires that CO or CO_2 be formed. This is impossible when IBr is the halogenating agent. That metaborate is not removed by reaction with hexa-bromobenzene is probably attributable to the low partial pressure of that reagent. Incomplete volatilization of BO_2^- in the starting material produces the lines of Figure 1.

Carbon tetrachloride is effective primarily for removal of impurities which lead to absorption at 1.06 and 10.6 μm.

Table 4 shows that KBr purified with its aid retains appreciable absorption at 2.7 and 3.8 μm. Hass (9) and Harrington, Gregory, and Otto (10) have shown that no method of purification has diminished absorption (in any material) at 2.7 and 3.8 μm to levels comparable to those measured at 1, 5, or 10 μm. The impurities responsible for these enhanced absorptions have not been identified. From present observations, it is unlikely that oxygenated impurites - especially hydroxyl ions - are solely responsible.

Table 5. Equilibrium Constants at $1000^{\circ}K$ for Reactions of Oxygen-Containing Impurities.

Reaction	Log K
$KClO_4 = KCl + 2\ O_2$	16.8
$K_2CO_3 + CCl_4 = 2\ KCl + CO + Cl_2 + CO_2$	24.0
$K_2SO_4 + CCl_4 = 2\ KCl + CO + Cl_2 + SO_3$	10.7
$2\ KBO_2 + CCl_4 = 2\ KCl + CO + Cl_2 + B_2O_3$	17.8
$KBO_2 + CCl_4 = KCl + BCl_3 + CO_2$	17.5
$KBO_2 + CCl_4 = KCl + BCl_3 + C + O_2$	-3.2
$KBO_2 + 2\ Br_2 = KBr + BBr_3 + O_2$	-14.5
$KBO_2 + 2\ IBr = 1/2\ KBr + 1/2\ KI$ $+ 1/2\ BI_3 + BBr_3 + O_2$	-22.8

V. CONCLUSION

To date, carbon tetrachloride is the only halogenating agent which has yielded KBr crystals with 10.6-μm bulk absorption coefficients as low as 0.00001 cm^{-1}. No adverse effects of the slight concomitant chloride contamination have been detected. When OH^- concentrations are less than 5 ppmA, presence of some other contaminant sets a lower limit on 10.6-μm absorption. Removal of this contaminant is more completely effected by exposure to CCl_4 than by treatment with the bromine-containing agents studied. Purity must be increased still further if 2.7-μm and 3.8-μm absorption are to approach correspondingly low values.

ACKNOWLEDGEMENT

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CHEMICAL POLISHING OF KBr

AND ABSORPTION MEASUREMENTS AT 1.06 µm

James W. Davisson
U.S. Naval Research Laboratory
Washington, D.C. 20375

ABSTRACT

A procedure for the chemical polishing of KBr in a solution of HBr is described. Surfaces of very high quality appear to be attainable using this procedure as evidenced by visual and microscopic inspection. The absorption coefficient of KBr and other alkali halides and alkaline earth fluorides has been obtained at 1.06 µm with absorption coefficients in the 10^{-5} cm^{-1} level and as low as 3×10^{-6} cm^{-1} in KBr.

INTRODUCTION

The surface finishing of infrared materials by chemical polishing is well known and specific procedures have been summarized (1). For KCl, chemical polishing in HCl was developed in this laboratory and appears to provide one method for the production of good stable surfaces with low absorption coefficients at both this (2,3) and other laboratories (4,5). Other chemical polishing agents such as weak organic acids have also been used (6). The extension of our polishing procedure to the crystal KBr by using HBr has now been carried out with very good results. Surfaces polished by this procedure appear to have very low scatter by visual inspection with a laser beam and also appear to be of excellent quality under Nomarski microscope inspection. Measured at 1.06 µm, a chemically polished KBr rod yielded a coefficient of absorption that was less than 3×10^{-6} cm^{-1}.

To the best of our knowledge very few absorption coefficients have been reported at 1.06 µm and the list given here in Table I is the first extensive collection we are aware of and the values are comparable in magnitude to the best fiber optic glasses (7).

TABLE I. BULK ABSORPTION COEFFICIENTS AT 1.06 μm

Crystal[a]	Source	Dimensions (cm x cm x cm)	Abs. Coeff. (cm^{-1})
LiF	Harshaw	1.3 x 1.3 x 10.3	6×10^{-5}
LiF	Optovac	1.3 x 1.3 x 10.3	8×10^{-4}
NaF	Optovac	1.3 x 1.3 x 9.8	5×10^{-4}
NaF	NRL #11	1.7 x 1.8 x 5.1	5×10^{-5}
NaF	NRL-96D	1.3 x 1.3 x 8.4	3×10^{-5}
NaCl	Harshaw	1.4 x 1.4 x 10.3	7×10^{-6}
KCl	NRL B-219	2 x 2 x 7.7	7×10^{-6}
KBr	NRL B-305	1.5 x 1.5 x 7.9	$<3 \times 10^{-6}$
KBr	NRL B-212	1.2 x 1.3 x 6	5×10^{-6}
CaF_2	Harshaw	1.3 x 1.3 x 10.3	6×10^{-5}
CaF_2	Optovac	1.3 x 1.3 x 10.3	1×10^{-5}
CaF_2	Hughes	1.0 x 1.0 x 7.45	4×10^{-5}
SrF_2	Harshaw	1.3 x 1.3 x 10.3	1×10^{-5}
SrF_2	Optovac	1.3 x 1.3 x 9.9	7×10^{-5}
BaF_2	Harshaw	1.3 x 1.3 x 10.3	3×10^{-5}
BaF_2	Optovac	1.3 x 1.3 x 10.3	1×10^{-5}

[a]The chlorides and bromides were chemically polished in HCl and HBr respectively. NaF was chemically polished in dilute $Mn(NO_3)_2$ + HF solution (See P. H. Klein and J. W. Davisson, Fourth Laser Window Materials Conf. p. 466). The alkaline earth fluorides and LiF were mechanically polished by rubbing till dry on Pellon Pan-W pad using Linde C with water as lubricant. The Hughes CaF_2 crystal was press-forged 86% at 900°C.

CHEMICAL POLISHING OF KBr

The procedure used to chemically polish KBr crystal was the same as that used previously to polish KCl and NaCl crystal (2) except that HBr was used as the polishing agent and isopropyl alcohol as the washing agent. The crystals of KBr employed were grown in a reactive atmosphere as described by P. H. Klein in an accompanying article. The processing of these boules was carried out as follows:

KBr rods (ca. 1 cm^2 x 6 cm), mechanically sawed from Bridgman boules, were chemically processed in three steps: - (a) They were first water ground on a Politex Supreme lap to remove surface damage (2). This produced a smooth but uneven surface (Fig. 1A). (b) An even but structured surface (Fig. 1B) was then obtained by manually agitating the crystal, situated in a platinum wire basket, 30 minutes in fuming HBr solution.
(c) A smooth chemically polished surface was then obtained (Fig. 1C) by immersing the sample 3 seconds in a diluted 50% solution of HBr.
Each of the above operations was terminated by removal of the solution with a jet of isopropyl alcohol and drying with warm air.

The quality of the surfaces such as shown in Fig. 1C was excellent. Showing no degradation upon standing in the open for more than a week, they imparted a wet appearance to the specimen and showed no evidence of steps or individual etch pits under the Nomarski microscope at 750X magnification. However this high quality was achievable only on surfaces that were remote from the (100) orientation. Surfaces that were vicinal to (100) yielded nonremovable steps as shown in Fig. 2.

ABSORPTION MEASUREMENTS AT 1.06 μm

Crystals of KBr and other alkali and alkaline earth halides were fabricated into rods typically 1 cm square and 6 - 10 cm long for the determination of the bulk absorption coefficient as described in previous articles from this laboratory (8). Here the initial slope of the thermal rise curve has been shown to be representative of the bulk absorption coefficient of the substance. Table I shows the bulk absorption coefficient of these materials at 1.06 μm using a Nd:YAG laser operating at 5 watts. The thermal rise curve for KBr is shown in Fig. 3 and a typical rise curve for the alkaline earth fluorides in Fig. 4. The absorption coefficient at 2.7 μm and at 3.8 μm of some of these rods was obtained at the Univ. of Alabama--Huntsville and is reported elsewhere in these proceedings and a discussion of the various results is summarized by Hass in these proceedings.
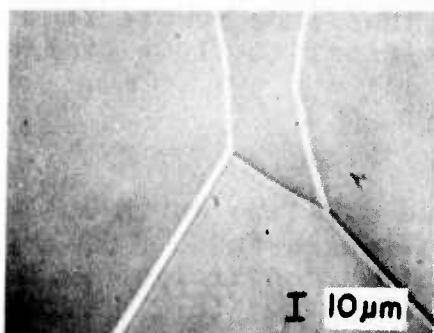
KBr

(A) AFTER WATER GRIND
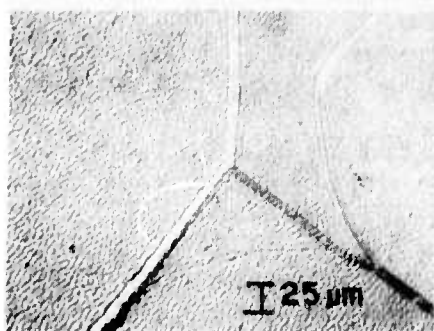
(B) AFTER FUMING HBr

(C) AFTER 50% HBr

Fig. 1. Chemical polishing procedure shown by Nomarski photomicrographs. (A) Water grinding, used to remove surface damage, left the surface smooth but uneven. (B) The surface was rendered even but textured after 30 min. agitation in turning HBr. (C) A smooth even surface was then obtained after a quick dip in 50% HBr solution.

KBr

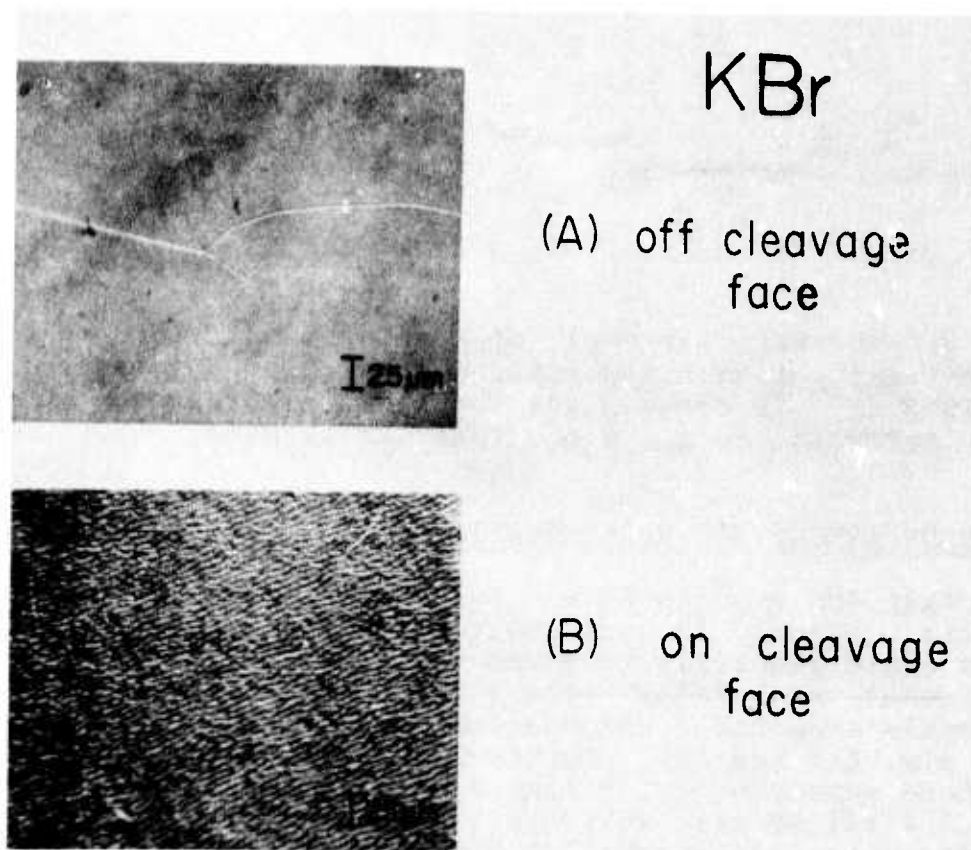**(A) off cleavage face**

(B) on cleavage face

Fig. 2 Orientation dependence of chemical polish on KBr crystals. (A) Smooth even surfaces were obtained only on faces remote to (100). (B) Surfaces vicinal to (100) showed a nonremovable texture.
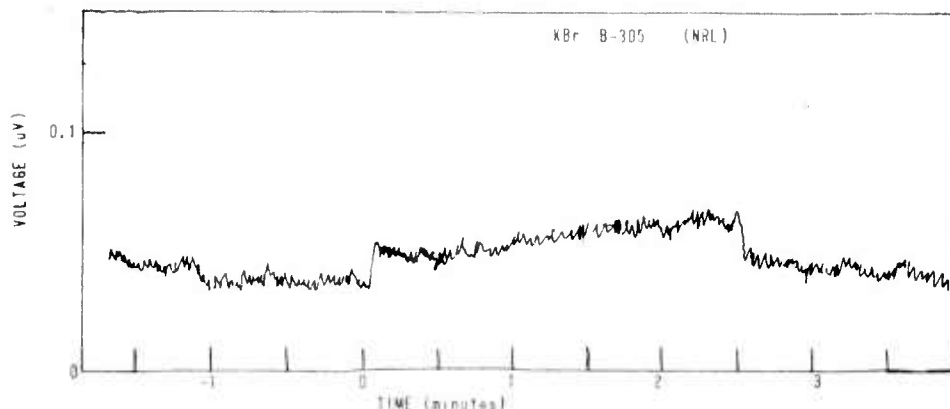
Fig. 3. Thermal rise curve of KBr for 5 watt 1.06 μm laser light. A bulk absorption coefficient not exceeding 3×10^{-6} cm^{-1} is deduced for this N.R.L. RAP grown, chemically polished, 50 g., 8 cm. long KBr crystal.

DISCUSSION OF ABSORPTION MEASUREMENTS

Basically the results on all these materials (Table I) are very similar. Namely, in just about all cases, absorption coefficients could generally be found to lie in the 10^{-5} cm^{-1} level with the lowest value being about 3×10^{-6} cm^{-1}. In a number of cases crystals from different sources showed markedly different results - e.g. LiF and NaF. Furthermore, in the course of carrying out these measurements, a number of interesting observations were made. First of all, in properly prepared crystals, little or no surface absorption could be detected by inspection of the slope of the thermal rise curves (Figs. 3 and 4). In those cases where appreciable absorption was found, flaws in the surface were evident by inspection with a visual laser beam. Cracks near an edge could be made visible by a laser beam well away from the imperfection. It is our impression that such imperfections might very well lead to corresponding absorption in a laser calorimetric determination.

A rough determination of the absorption coefficient at 10.6 μm of one of the KBr rods (B-212) led to a value of 6×10^{-5} cm^{-1} which is believed to be the lowest reported at this wavelength. A subsequent KBr crystal (B-305) showed very low absorption at 1.06 μm which was essentially unmeasurable (Fig. 3). At 10.6 μm Harrington and Rowe, elsewhere in these proceedings, indicate a bulk absorption coefficient for KBr in the range of 2×10^{-5} cm^{-1} and a surface loss less than 0.1% over the entire tuneable 10.6 μm region. While this has only been obtained in one crystal, the results are quite encouraging and suggest that both the bulk and surface absorption of KBr can be reduced to lower levels than in KCl

when these crystals are RAP grown and chemically polished in the manner described.
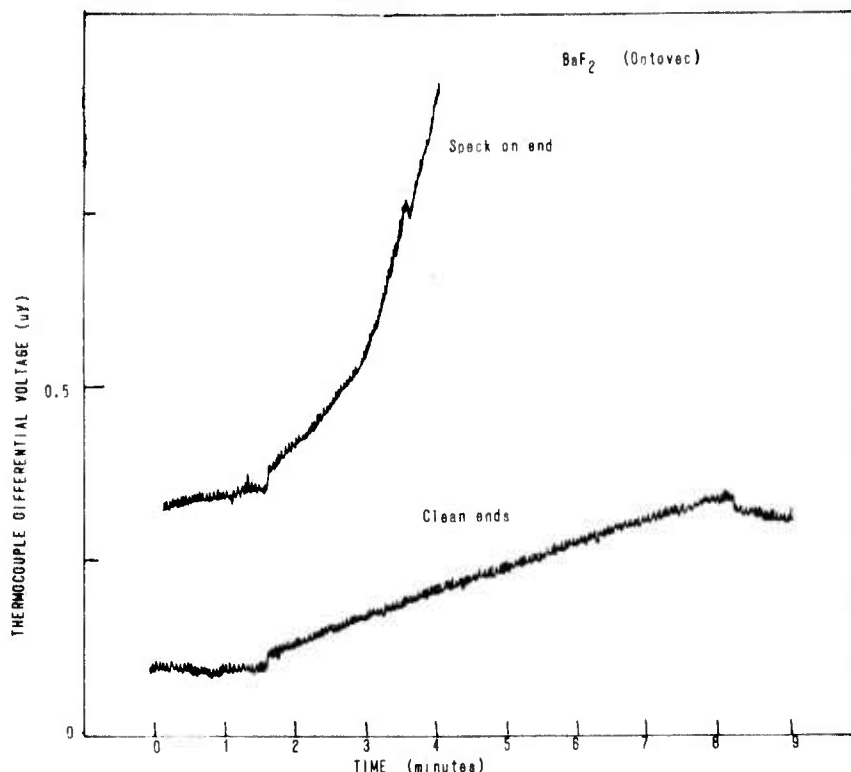
Fig. 4 Thermal rise curves showing typical behavior of the alkaline earth fluorides for 1.06 μm laser light at 5 watts power. The typical lower curve shows a linear rise which indicates negligible end-face heating. The upper curve shows the effect of end-face heating produced by a speck of dust. For the example shown the bulk absorption coefficient, obtained from the initial slope, is 0.000011 cm^{-1} for the lower curve and 0.000016 for the upper curve (difference may not be significant). The total absorption (surface and bulk) obtained from the slope at longer times is 0.000011 cm^{-1} for the lower curve and 0.00022 cm^{-1} for the upper curve.

CONCLUSION

A procedure for chemical polishing of KBr has been developed which appears to give surfaces of high quality and low loss.

Absorption coefficients at 1.06 μm in the range of 10^{-5} cm^{-1} have been observed in a variety of alkali halides and alkaline earth fluorides.

ACKNOWLEDGMENT

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Infrared Bulk and Surface Absorption
by Nearly Transparent Crystals*

Herbert B. Rosenstock
Naval Research Laboratory
Washington, D. C. 20375

and

Don A. Gregory and James A. Harrington
University of Alabama
Huntsville, Alabama 35807

We present an analysis of laser calorimetric data which deduces both
the bulk and the surface absorption in a single run. The method involves
use of long rod geometry combined with an analytical solution of the heat
equation for the temperature distribution in a sample that is heated both
internally and on the surfaces. Bulk and surface absorption coefficients,
heat transfer coefficient, and thermal diffusivity appear as parameters;
the last is treated as known, and the thermal rise curve is fitted to the
three others. The solution obtained is valid at all points and times, and
measurement of the temperature during and after laser heating at
different points therefore narrows the possible fit considerably. Examples
illustrating the method are presented for .ZnSe, CaF_2, NaF:Li, NaCl,
KBr and KCl at 2.7, 3.8 and 10.6 microns. Surface absorption is found
to be dominant in almost all cases.

I. Introduction

We have measured the absorption of several almost transparent crystals at several infrared frequencies (see Table 1). On account of the weakness of the absorption, the usual direct spectroscopic method, which involves comparison of the intensities of the incoming and outgoing beams, fails and "laser calorimetry" techniques must be used: what is measured at a certain point on the crystal is the temperature rise as a function of time while, and after, the sample is penetrated by a laser beam; this can then be related to the absorption coefficients of the material. That relationship is not wholly straightforward, but sufficiently careful analysis enables us to determine separately both the bulk absorption coefficient and the total absorption at the surfaces. In all cases, we have found the latter to dominate - a consequence, undoubtedly, of the considerable care that has been taken in purifying and perfecting the crystals, thus probably reducing the bulk absorption close to its "intrinsic" or "multiphonon" minimum. As the practical motivation for this work is the discovery and preparation of highly transmitting solids (for applications such as windows to a high power laser), the fact that surface rather than bulk absorption is now dominant even for fairly thick crystals is an important one in guiding further efforts.

In Section II we describe our method of analyzing data, show its relation to the more usual simpler techniques and explain why we believe that the extra effort is worthwhile and indeed essential. In Section III we describe our experimental arrangements and our results, and in Section IV we discuss their significance. The Appendix contains the dry mathematical detail needed for Section II.

II. Analysis: Temperature Distribution

We need the solution to the following problem in heat conduction: a solid, originally at a uniform temperature, is heated by a source constant in time from time $t=0$ to time $t=t_1$; find the temperature at all points and times. This is a classical boundary value problem whose solution is outlined in at least one

standard textbook.[1] But, in spite of a recent resurgence of interest[2-4], we have found no detailed solution of this precise problem suitable for our purposes, and we therefore present it here.

First, however, let us consider the "usual" simple procedure for inferring absorption coefficients from laser calorimetry data (i. e. temperature vs. time curves). There, one assumes "small" samples and neglects heat losses to the environment; more precisely, it is assumed that absorption of energy anywhere in the sample results instantaneously in a temperature rise that is uniform throughout the sample. The slope of the resulting thermal rise curve alone (rather than the detailed shape of the curve) is then analysed to yield an average absorption coefficient. This simple procedure ignores all space-dependence of the temperature and thus implicitly assumes immediate thermalization (the heat absorbed is supposedly dispersed uniformly through the sample, and in a time shorter than of experimental resolution). Much obtainable information is in effect discarded when experimental conditions make that assumption valid. For example, by actually measuring temperature differences as function of position (rather than assuming that none exist), we can learn about the source of the heat (e. g., bulk vs. surface absorption), particularly in samples that are long or thin. The simple analysis is also invalid at very short times (before thermalization can occur) or very long ones (after heat transfer across the boundary is important). Our detailed analysis, which explicitly gives the temperature as a function of both position and time, is therefore particularly useful for irregular geometries (e. g., samples that are "long" or "thin"), and for experiments in which time resolution is good.

Accordingly, we solve explicitly the heat equation

$$[\nabla^2 + g/k] \, T = (1/\alpha) \, \partial T/\partial t \tag{1}$$

subject to the boundary conditions

$$k \, \partial T/\partial n + h T = 0 \qquad \text{(all boundaries)} \tag{2}$$

21

and the initial condition

$$T = 0 \qquad\qquad (t = 0) \qquad\qquad (3)$$

at all points in the solid. Here t means time, x, y, z, are the space co-
ordinates, $T = T(x, y, z, t)$ is the temperature, k the thermal conductivity,
$\alpha = kc/\rho$ is called "thermal diffusivity", c and ρ are the specific heat and
density of the solid, h is the heat transfer coefficient (the rate at which heat
is lost across the surface) n is the space normal at any point on the surface
and $g(x, y, z, t)$ the source of heat (in our case the heat absorbed from the
laser beam traversing the solid). Our general boundary conditions (called
"boundary conditions of the third kind") reduce to simpler ones when h/k
approach either 0 ("second kind" - insulated surfaces) or infinity ("first kind" -
a heat bath). Explicit solutions of this system can be obtained for certain
coordinate systems (we have done so in rectangular and cylindrical ones) and
for certain forms of the source function g; the forms of g for which this is
possible are fairly restrictive, but correspond closely to what we need in
practice. The first restriction we put on g is on its time dependence: the
source must be either on or off, and not vary with time in any more compli-
cated way:

$$g(x, y, z, t) = \begin{cases} g_o(x, y, z) & 0 < t < t_1 \\ 0 & \text{otherwise.} \end{cases} \qquad (4)$$

g_o can contain both surface and bulk terms, but to allow proceeding
further in closed form, the beam profile - i.e., the y, z-dependence of g_o -
must be somewhat restricted. We have found three such profiles. They are a
delta function (i. e., an infinitely sharp beam), a step function (i. e., a beam of
uniform intensity near the center and 0 elsewhere) and narrow gaussian
("narrow" in the sense that its halfwidth must be appreciably smaller than the
cross section of the absorber). Let us write out only the first of these forms:

$$\dot{q}_0 = P\left\{\beta + \tfrac{1}{2}S\left[\delta(x) + \delta(x-L_x)\right]\delta(y - \tfrac{1}{2}L_y)\delta(z - \tfrac{1}{2}L_z)\right\} \quad (5)$$

This describes a sharp beam of power P traversing a rectangular parallele-piped along its x-axis; the solid extends through $0 < x < L_x,\; 0 < y < L_y,\; 0 < z < L_z$. Integration of (5) over the entire solid verifies that β and S are, respectively, the bulk absorption coefficient (per centimeter) and total fractional absorption by both surfaces (dimensionless). The results are written out in the Appendix and in more detail in Ref. 5. For present purposes, we can write the temperature simply as

$$T(x,y,z,t) = \beta\sum_m\sum_n\sum_p f^{(1)}_{mnp}(x,y,z,t) + S\sum_m\sum_n\sum_p f^{(2)}_{mnp}(x,y,z,t) \quad (6)$$

The point is that the bulk and surface absorption β and S appear simply as multiplicative constants; the f's are known (though fairly complicated) functions depending on the physical parameters $\rho, k, C,$ h and the crystal dimensions as well as the indicated space and time coordinates; the sums over m, n, p contain an infinite number of terms but converge reasonably rapidly. The result appears in the same form for other beam profiles (only the details of the f's are different); and the same is true for cylindrical absorbers (in which case the space coordinates should be called (r, z) rather than (x, y, z) and there are only two instead of three summations).

The procedure for making measurements is now as follows: attach a thermocouple to a point (x, y, z) of the solid; measure T there from time 0 (laser turn-on) to some time beyond t_1 (laser cutoff); attempt to fit the resulting curve to (6) above by varying the bulk and surface absorption constants β and S, thus determining the latter when a fit is obtained. The procedure should then be repeated for placement of the thermocouple at some other point (x, y, z); a different curve will be obtained, but it should be fittable by the same β and S. We should also mention one unpleasant complication: One of the parameters

entering into the f's in (6), viz., the heat transfer coefficient h, is not usually known, and so must be treated as an unknown, together with β and S, in the fitting process.

III. Experimental Techniques and Procedures

Standard laser calorimetric methods[6] were employed to measure the small absorption coefficients at chemical laser frequencies. The experimental set-up, which has been described elsewhere in greater detail[7] consists of an air calorimeter and a small CW DF-HF chemical laser of our own construction.[8] The calorimeter is conventional, see Figure 1, except for a series of small holes along the bottom which admit a purge gas (dry nitrogen, helium, etc.). In practice, the absorption of HF radiation by air in the calorimeter and subsequent distortion of the heating-cooling curves due to heating of the air has not been detected even without the purge. Purge gas is frequently used, however, to minimize any errors in the temperature-time data and to better characterize the heat transfer coefficient which is of importance in the theoretical prediction of the temperature-time curves.

The samples studied have been procured from a wide variety of window material processors. The contributors in this case were the Naval Research Laboratory, Harshaw Chemical Company, and Raytheon Corporation. In most cases, the samples are received with a good surface finish. When this is the case, the samples are run as received. After an initial measurement, the surfaces are examined using Normarski microscopy and then refinished. Mechanical polishing involves a final polish with Linde B and isopropanol with intermediate polishes using diamond grit for the harder substances. For ZnSe the prescriptions of Hughes Research Lab[9] and Raytheon[10] for chemical etching on pitch laps were utilized.

Surface cleaning just prior to measurement is one of the most important requirements for a reliable absorption coefficient. Crystals washed with CH-bonded solvents like methanol, ethanol, acetone, etc. which have absorptions[11] in the DF-HF region show higher absorption coefficients than crystals washed in,

for example, carbon tetrachloride. At present, all samples have a final cleaning with spectrograde CCl_4 just prior to measurement.

Measurements were made on several crystals and three frequencies. A sample of the data is shown in Fig. 2. Here the solid curves are the experimental measurements on a ZnSe sample about 6 x 1 x 1 cm in size; the points are the "best" fit obtainable by varying the parameters h/k, β and S. All other parameters are treated as known[12,13]. The upper curve is a run taken with the thermocouple at the center of the surface (x=3 cm), the lower one with the thermocouple near the end (x=1 cm). In course of the analysis, h/k is first determined by fitting to the curve beyond the laser cutoff (because at those times, no further absorption is taking place and the changes in temperature are therefore largely due to the surface heat losses and no longer strongly dependent of the other unknowns, β and S. Then the early parts of the curves are fitted by varying the bulk and surface absorption coefficients. Once this is optimized, further improvements are usually possible by changing h again and repeating the process. The reader will note that very good fits are possible to either curve, but not to both simultaneously with the same parameters. This, of course, points to the importance of making temperature measurements at more than one point if convincing values of the absorption coefficients are to be obtained. Results are summarized in Table 1.

IV. Discussion

In discussing our data as summarized in Table 1, let us first consider the last column which gives the heat transfer coefficient (divided by the presumably known thermal conductivity). This is not a quantity of primary interest to us, but must be determined because it is not available in the literature. It has two components, a radiative and a convective one, of which the latter is believed to be the more important. It is also the latter one which is most uncertain and probably responsible for the wide variations in the third column. It would appear that convection currents arise inside the calorimeter, unpredictably, at some times and not at others. Furthermore, the great changes in the effective heat transfer coefficients from one run to the next also suggest the likelihood of variations during one run, in contradiction to the implied assumption in our derivation that the heat transfer is a constant in any one run. Two conclusions

25

must therefore be drawn from the large variations shown in the last column of Table 1: First, that the results in the other two columns, which are of greater physical interest, are not wholly reliable either, on account of the unpredictable variations in the heat transfer coefficient (although we should in fairness point out that the data are much less sensitive to changes in the heat transfer coefficient than they are to changes in the absorption coefficients); and, second, the importance of working in the future with an evacuated calorimeter in which the convective and variable heat transfer coefficient will be reduced to nearly zero and only the radiative part which indeed should remain constant will be left. In one case, KBr at 2.7 microns, we were able to reduce the heat transfer coefficient to a point at which it was no longer troublesome, by filling the calorimeter with He rather than air.

The first two columns of numbers, the bulk and surface absorption coefficients, also show considerable variation and should therefore be considered as tentative. Nonetheless, certain physically realistic conclusions can be drawn. The major one is the dominance, at all three frequencies, of surface effects. In every case, the total surface absorption is considerably larger than the bulk absorption of several centimeters of crystal. One point that does not appear clearly from Table 1 but must be made plain here is the dependence of our results not only on the substance used, but on the particular crystal; variations, not shown in Table 1, were obtained for crystals of nominally the same composition, but different preparation and surface treatment. The fact that in each case the surface absorption is equivalent to many cm of bulk absorption indicates that the overall success of growing pure crystals in bulk has been considerable, and that improving the surface quality of crystals is now the most important task before us towards the goal of producing substances whose overall absorption will be minimal.[14]

Appendix - A Particular Solution to the Heat Equation

In Section II, the appropriate heat flow problem was formulated and the solution given schematically. Here we summarize the details.

The solution is

$$T(x, y, z, t) = (P/k) \sum_m \sum_n \sum_p \left[Z_m^2 Z_n^2 Z_p^2 / \gamma_{mnp} \right] \cdot$$
$$\cdot u(\varepsilon_m, x)\, u(\varepsilon_n, y)\, u(\varepsilon_p, z) \cdot$$
$$\cdot (P_1 \beta + P_2 S)\, u(\varepsilon_n, L_3/2)\, u(\varepsilon_p, L_2/2)$$
$$\cdot \psi_{mnp}(t)$$

Here P is the power of the laser beam $H = h/k$,

$$\psi_{mnp}(t) = \begin{array}{ll} 1 - e^{-\alpha \gamma_{mnp} t} & 0 < t < t_1 \\ e^{-\alpha \gamma_{mnp} t} \left[e^{+\alpha \gamma_{mnp} t_1} - 1 \right] & t > t_1 \end{array}$$

$$P_1 = (H/\varepsilon_m)\left[1 - \cos L_x \varepsilon_m \right] + \sin L_x \varepsilon_m$$
$$P_2 = \varepsilon_m \left[1 + \cos L_x \varepsilon_m \right] + H \sin L_x \varepsilon_m$$

and L_x is the length of the sample.

The ε_m are the positive solutions of

$$\tan \varepsilon L_x = 2 H \varepsilon / \left[\varepsilon^2 - H^2 \right]$$

and the $u(\varepsilon_m, x)$ and Z_m are given by

$$u(\varepsilon_m, x) = \varepsilon_m \cos \varepsilon_m x + H \sin \varepsilon_m x$$
$$Z_m^2 = 2 / \left[2H + L_x (\varepsilon_m^2 + H^2) \right]$$

27

To obtain the ξ, u, and Z with subscripts n (or p) instead of m, replace x by y (or z) in the above expressions. The reader should consult Ref. 5 for solutions applicable to other situations (to sources other than the g_0 of (5), and to cylindrical geometries); and Ref. 1 for more general theory of the heat equation.

Acknowledgements

TABLE 1

	BULK ABSORPTION COEFFICIENT (cm^{-1}) 10^5 β	SURFACE ABSORPTION (DIMENSIONLESS) 10^5 S	HEAT TRANSFER COEFFICIENT (cm^{-1}) 10^3 h/k
2.7 MICRONS			
KBr	5	190	1
ZnSe	50-140	60-900	2
CaF2	20	350	20
NaF:LiF	80	350	4
3.8 MICRONS			
ZnSe	110	280	1-2
CaF2	25	270	32
NaCl	90	4000	60
10.6 MICRONS			
KBr	12	420	1
KCl	8	90	2

Bulk absorption coefficient and total surface absorption of several crystal at three wavelengths.

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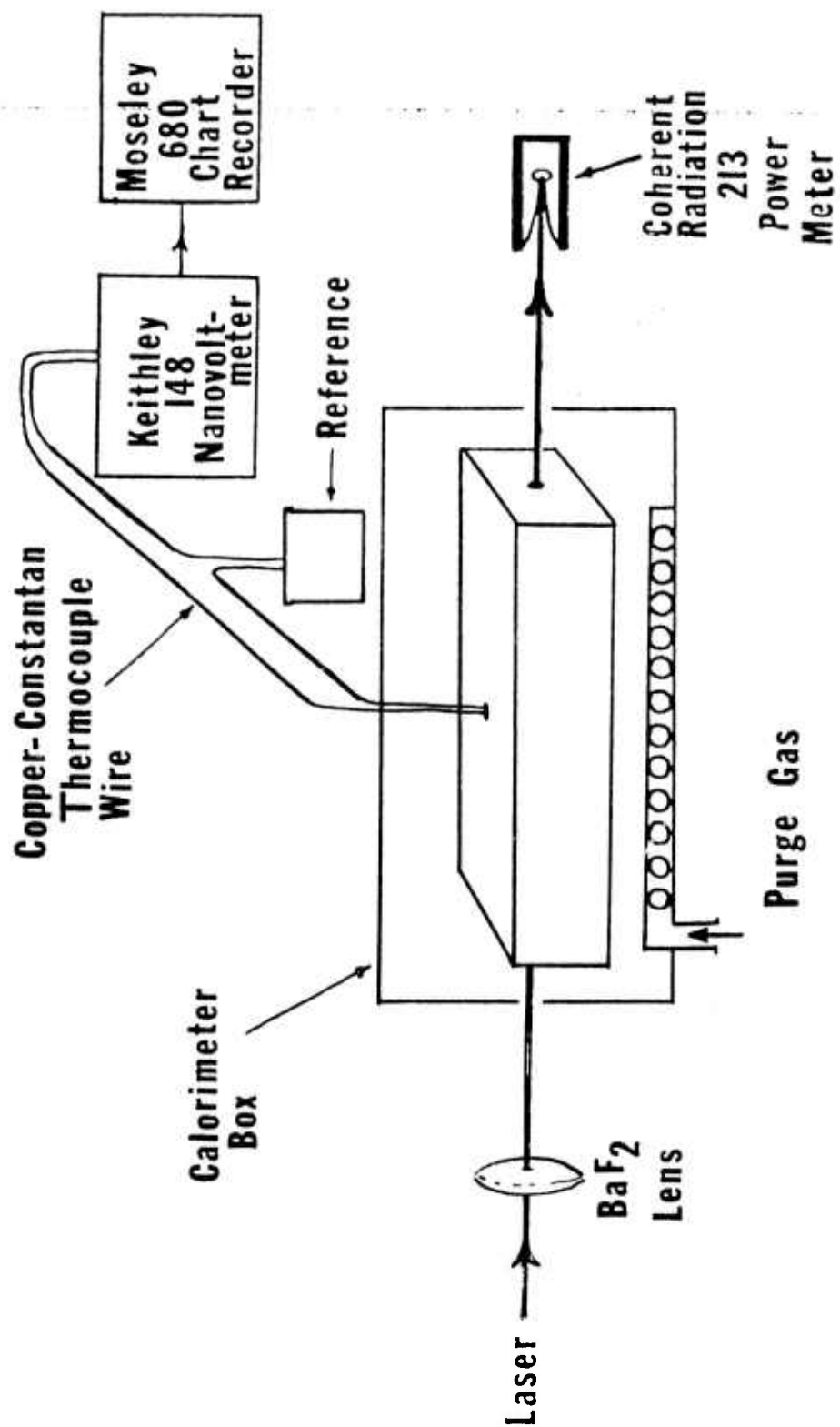14. J.W. Davisson, J. Materials Science 9, 1071 (1974).

Figure 1. Schematic experimental arrangement.

Laser

BaF_2 Lens

Calorimeter Box

Copper-Constantan Thermocouple Wire

Keithley 148 Nanovolt-meter

Moseley 680 Chart Recorder

Reference

Purge Gas

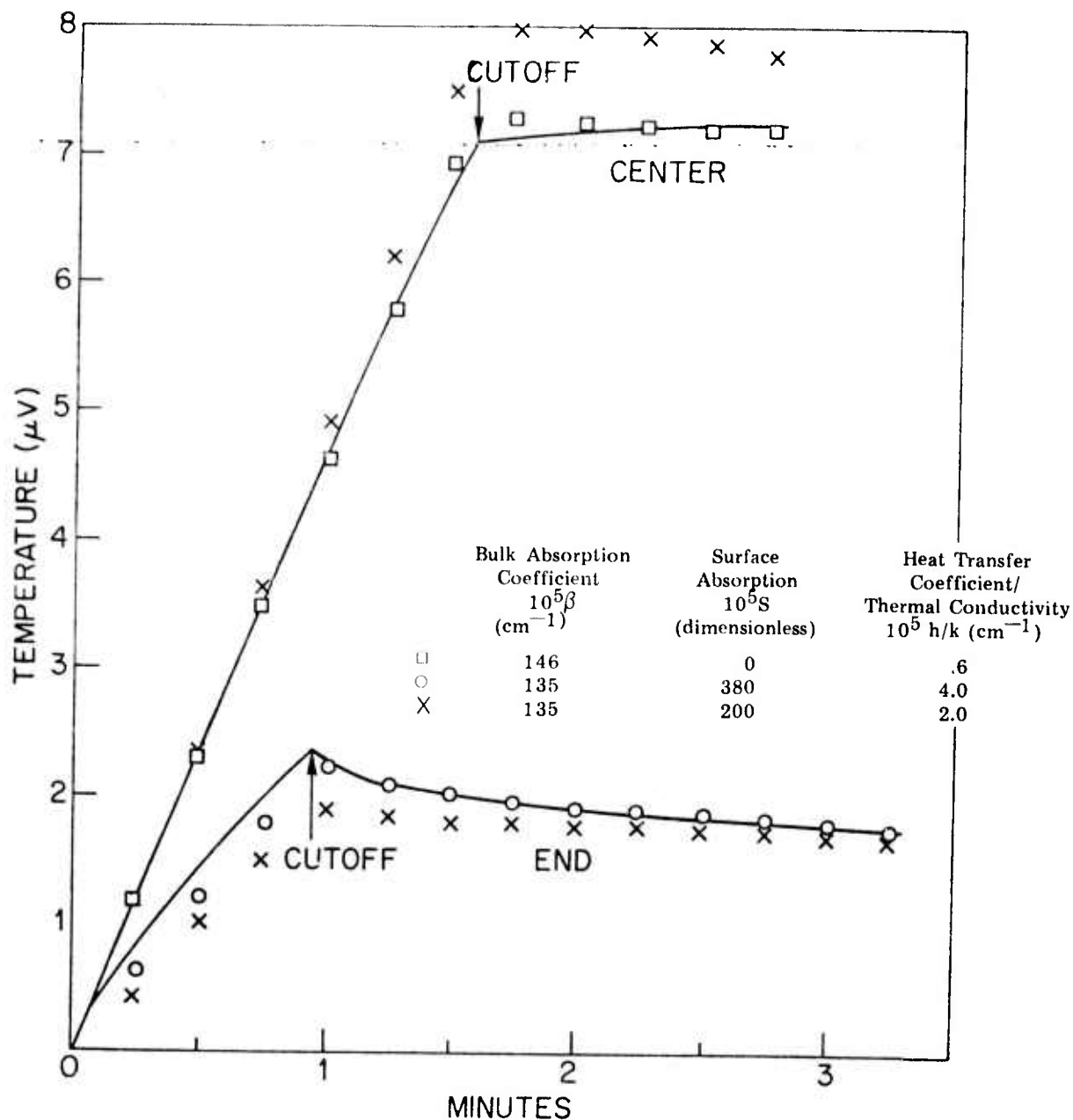Coherent Radiation 213 Power Meter

Figure 2.   Sample of data. (ZnSe at 2.7 microns). Solid curves are experimental result; the upper for measurement at the center of the lateral surface, the bottom for measurement on a point on the lateral surface near an end surface. Individual points indicate attempted analytical fits by Eq. (6). While excellent fits are obtainable for each curve separately (squares and circles, respectively, the best to both curves (crosses) shows 10% deviations.

FRACTURE BEHAVIOR IN ALKALINE EARTH
FLUORIDES[+]

S.W. Freiman, P.F. Becher, R.W. Rice, and K.N. Subramanian[*]
U.S. Naval Research Laboratory
Washington, D.C. 20375

ABSTRACT

Experimental studies show that the average critical fracture energy (IC) for {111} cleavage crack propagation in the $\langle 110 \rangle$ direction in CaF_2, SrF_2, and BaF_2 crystals is 0.51, 0.42 and 0.30 J/m^2 respectively. The value of IC in CaF_2 increases to 0.8 J/m^2 when the crack direction is changed to the $\langle 112 \rangle$. In comparison, alkali halide crystals exhibit IC values for {100} cleavage crack motion $\langle 100 \rangle$ of ~ 0.25 J/m^2 at comparable loading rates. Crack propagation in alkaline earth fluorides differs from alkali halides in several ways: 1) IC decreases with reduced crack velocity, 2) moisture-enhanced slow crack growth accompanied by crack arrest is observed, and 3) only limited plastic deformation is associated with crack propagation.

The measured fracture energy of large grained (1-10 mm) polycrystalline CaF_2 is 1.6 J/m^2 for transgranular {111} crack propagation, i.e. closer to that for single crystal {111} fracture than the ~ 3.6 J/m^2 value for fine grained (~ 50 μm) CaF_2. Examination of the polycrystalline fracture surfaces of fusion cast and press forged CaF_2 and SrF_2 bend test specimens shows that fracture initiation often occurs within a single large grain, typically several hundred microns in size. Fracture energies calculated from the failure stresses and flaw sizes averaged ~ 1.6 J/m^2 in agreement with the measured value of large grained bodies. Thus, fracture within a single large grain appears to control the strength of these materials.

Most fracture origins in these polycrystalline fluorides were from the surfaces, often from edges, indicative of the common problem with finishing edges. However, as flexural strengths are increased over 15,000 psi with improved surface finish and/or annealing, the position of the fracture origin shifts from the tensile surface to the interior. Because the actual tensile fracture stress decreases as the fracture origin moves into the interior of a bend test specimen, the actual stress at the flaw will be somewhat less than that calculated.